POLITECNICO DI TORINO
Repository ISTITUZIONALE

Modelling the swelling and osmotic properties of clay soils. Part I: The phenomenological approach

Original
Modelling the swelling and osmotic properties of clay soils. Part I: The phenomenological approach / Dominijanni, Andrea; Manassero, Mario. - In: INTERNATIONAL JOURNAL OF ENGINEERING SCIENCE. - ISSN 0020-7225. - STAMPA. - 51:(2012), pp. 32-50. [10.1016/j.ijengsci.2011.11.003]

Availability:
This version is available at: 11583/2422556 since:

Publisher:
Elsevier

Published
DOI:10.1016/j.ijengsci.2011.11.003

Terms of use:
openAccess

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

05 May 2023

Modelling the swelling and osmotic properties of clay soils: Part I. The phenomenological approach

by

Andrea Dominijanni* and Mario Manassero**

* *Corresponding Author*

Dipartimento d'Ingegneria del Territorio, dell'Ambiente e delle Geotecnologie [Land, Environment and Geo-Engineering Department], Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino – ITALY; Ph: +39-011-090-7705, Fax: +39-011-090-7699, Cell Ph: +39-3387778804; e-mail: andrea.dominijanni@polito.it

** Dipartimento d'Ingegneria del Territorio, dell'Ambiente e delle Geotecnologie [Land, Environment and Geo-Engineering Department], Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino – ITALY; Ph: +39-011-090-7705, Fax: +39-011-090-7699, e-mail: mario.manassero@polito.it

DRAFT

ABSTRACT

Clay soils with a high montmorillonite content in their mineralogical composition are characterized by swelling and osmotic properties like biological tissues and polyelectrolyte gels. These phenomena are caused by the very high specific surface (≈ 760 m^2/g) and the negative electric charge of montmorillonite lamellae, which determine an interaction with the charge of the ions present in the pore solution. The interest in modelling the behaviour of such soils is related to the evaluation of their performances as hydraulic and contaminant barriers in landfill and soil remediation applications. The theoretical approach of the thermodynamics of irreversible processes is applied to find suitable phenomenological constitutive equations, under the assumptions of a unidimensional geometry, infinitesimal strains of the solid

skeleton and isothermal conditions. The approach is related to a saturated porous medium, whose voids are filled by an electrolyte solution containing an unspecified number of ions. To make the approach purely phenomenological, the parameters introduced into the constitutive equations are expected to be measured by macroscopic experimental tests, without any specification of the physical and chemical phenomena that occur at the pore scale. The constitutive equations allow the coupled transport and consolidation problem to be formulated for a clay barrier.

KEY-WORDS: clay barrier, thermodynamics of irreversible processes, porous media theory, chemical osmosis, swelling soils.

DRAFT

INTRODUCTION

Over the last few years, increasing efforts have been devoted to developing alternative barriers for liquid and contaminant containment to traditional compacted clay layers, in order to obtain higher performances and reduce construction problems and costs.

To this aim, the geosynthetics industry has put the so-called geosynthetic clay liners (GCLs) on the market. These are factory manufactured liners that consist of a thin layer of bentonite (~5-10 mm thick) which is generally sandwiched between two geotextiles (Bouazza, 2002).

Bentonite is a clay soil that usually contains at least 70% of the three layered (2:1) clay mineral montmorillonite. Isomorphic substitution in montmorillonite usually results in the replacement of a portion of the tetravalent silicon (Si^{4+}) and the trivalent aluminium (Al^{3+}) in the crystalline structure with metals such as magnesium (Mg^{2+}), having a lower valence; this causes a permanent negative surface charge. Montmorillonite crystals consist of parallel-aligned elementary alumino-silicate lamellae, which are approximately 10 Å thick and 1000-2000 Å wide, and this results in a very high specific surface ($\approx 760\ m^2 \cdot g^{-1}$).

As an alternative to GCLs, bentonite can be mixed with sand or clay to construct thicker liners: in this case, the advantage of the easy installation of GCLs is lost, but a higher shear strength can be obtained for the liner.

Compacted bentonite liners are also considered for the final disposal of nuclear waste, since they are expected to maintain their barrier performances for centuries.

The evaluation of the performance of bentonite as a liquid and contaminant barrier requires an adequate theoretical approach that is able to model the simultaneous migration of water and solutes, and to account for the deformations of the solid skeleton.

The electric interaction between the montmorillonite lamellae and the ions contained in the pore solution, in fact, generates macroscopic phenomena that cannot be modelled with the classical constitutive equations of soil mechanics (Mitchell, 1993).

DRAFT

For instance, when a bentonite layer is put in equilibrium with an electrolyte solution, swelling or shrinkage is observed depending on the salt concentration, without any apparent modification of the effective stresses. Moreover, if a bentonite layer is interposed between two electrolyte solutions with different salt concentrations, a volumetric flux of water can be observed, even in the absence of a hydraulic gradient.

The mechanical and transport behaviour of bentonites has more affinity with that of biological tissues, reverse-osmosis membranes, or polyelectrolyte gels than with that of sands or gravels.

From a historical point of view, a large number of theories has been proposed to model the behaviour of such materials. A first fundamental distinction can be made between two theoretical approaches that are very different in their goals and which, opportunely combined, can be considered complementary.

The first approach is called *phenomenological* because it is finalized to describe how the phenomena occur, at the macroscopic scale of observation, without explaining why.

The second approach is called *physical* because it has the scope of explaining macroscopic phenomena on the basis of a conceptual picture of the physical and chemical interactions that occur at the pore scale.

This paper is focused on the first approach with the aim of formulating the constitutive equations that govern the behaviour of bentonite at the macroscopic scale. In a companion paper (Dominijanni and Manassero, 2011), a specific physical model, based on the Donnan theory of equilibrium between membranes and electrolyte solutions (Donnan, 1911), is applied in order to interpret the phenomenological parameters.

The reference problem concerns a horizontal clay liner that separates two electrolyte solutions containing different concentrations of ions (Fig. 1). The electrolyte solution at the top of the clay liner represents the leachate of a landfill, while the electrolyte solution at the bottom of the liner represents the aquifer underneath. The ion concentrations in the leachate are

DRAFT

generally higher than in the groundwater, therefore a difference in ion concentrations is expected to establish across the liner. The same geometry can be rotated to a vertical position in order to represent a cut off wall built for the incapsulation of a contaminated site.

DRAFT

PHENOMENOLOGICAL APPROACH

The difficulty in identifying the chemical and physical mechanisms that govern the interaction of montmorillonite lamellae and pore fluids at the microscopic scale was the historically practical reason that motivated the development of a phenomenological approach, based simply on the experimental observations of the phenomena at the macroscopic scale (Philip and Smiles, 1982; Neuzil, 1986; Smiles, 2008). The theoretical framework for such an approach was given, at the middle of the twentieth century, by the thermodynamics of irreversible processes (TIP), a non-equilibrium theory based on the postulate of local state, which stipulates that the present state of a homogeneous system, in any evolution, can be characterized by the same variables as at equilibrium, and is independent of the rate of evolution. TIP was introduced by Eckart (1940 a,b), and successively developed by Prigogine (1947), Meixner and Reik (1959), and De Groot and Mazur (1962). The theory has mainly been applied to fluids and is able to incorporate specific constitutive laws, such as Fourier's law of thermal diffusion, Navier-Stokes' law of viscosity and Fick's law of diffusion, in a consistent thermodynamic scheme.

Staverman (1952) was the first to apply the formalism of TIP to membrane processes. He considered a system in which the membrane was a discontinuity between two compartments containing an electrolyte solution at the same temperature (Fig. 2). A steady non-equilibrium condition can therefore be reached between the two compartments due to the presence of such a discontinuity in the system. In Staverman's original conceptual picture, the membrane was not a porous medium of finite thickness, but only a thermodynamic discontinuity between the two bulk solutions. The main result of Staverman's analysis is that the solvent and ion mass fluxes can be expressed as linear functions of the differences in the electro-chemical potentials of the liquid components contained in the two compartments.

DRAFT

The extension of Staverman's analysis to a porous medium poses at least two problems: the first concerns the evaluation of the state variables of a liquid phase, i.e. the ion concentration, c_i, the hydraulic pressure, u, and the electric potential, ψ, within the porous medium; the second regards the inclusion of solid skeleton deformations.

The first problem is probably the less obvious, and is due to the fact that when a charged porous medium is put in contact with a bulk electrolyte solution an equilibrium condition is reached, after a sufficiently long time: in this condition, the state variables are discontinuous between the bulk and the pore solution. This phenomenon is called *partition effect* (Yaroshchuk, 1995) and is caused by interaction between the solid skeleton and the liquid components at the microscopic scale. As a result, the macroscopic liquid state variables in the porous medium are determined by the mechanisms that occur at the pore scale and which, in a phenomenological approach, do not have to be specified. A solution to this problem was given by Spiegler and Kedem (1966), who introduced the so-called *virtual variables*. They imagined cutting the porous medium into a series of elements of length dx in the transport direction and interposing a virtual or equivalent bulk solution, which is in thermodynamic equilibrium with the adjacent element of the porous medium, between them (Fig. 3). In such a way, they were able to reproduce the same conditions of the system studied by Staverman for an infinitesimal element of the membrane, with the only difference being that the mass fluxes resulted to be linear functions not of the differences, but of the gradients of the electro-chemical potentials of the virtual electrolyte solution components. Introducing such virtual solutions can seem to be a theoretical trick to avoid the evaluation of the partition effect, but it should be pointed out that this is the only correct way of proceeding with the thermodynamic approach because, in this context, it is not possible to specify any physical property of the porous medium, since the description of the system is purely phenomenological. The consistency of the approach is given by the fact that the virtual solutions coincide with the

DRAFT

real ones at the boundaries of the porous medium: therefore, the problem formulated in terms of virtual variables can be coupled with suitable boundary conditions, expressed as functions of the liquid state variables in the external bulk solutions in contact with the porous medium.

In the following, the ion concentration, hydraulic pressure and electric potential of the virtual electrolyte solutions are indicated as c_i ($mol \cdot m^{-3}$), u ($N \cdot m^{-2}$) and φ (V), respectively. To avoid confusion with the virtual variables, the real variable symbols are marked with a line $(\overline{c}_i, \overline{u}, \overline{\varphi})$.

The second problem that has to be addressed in order to extend Staverman's approach to porous media is that of accounting for solid skeleton deformations. This problem is of central importance in the porous media theory, but is considered less in chemical literature.

A first mechanical theory for porous media, whose pores are saturated by a liquid, was given by Biot (1941), under the assumption of infinitesimal strains of the solid skeleton. Successively, finite strains were included by Gibson et al. (1967), Raats and Klute (1968a, 1968b), Smiles and Rosenthal (1968) and Biot (1972 and 1977), through the adoption of a Lagrangian coordinate system that moved with the solid skeleton.

The porous media theory was derived using the formalism of the thermodynamics processes by Coussy (1995). De Boer (2000; 2005) and Ehlers (2002) adopted the mixture theory approach of Truesdell and Tupin (1960) and the exploitation of entropy inequality of Coleman and Noll (1963) in order to derive constitutive equations for mechanical behaviour. Recourse was also made to the mixture theory in Rajagopal and Tao (1995) in order to couple mechanical and hydraulic behaviour.

Coupling of mechanical and chemical behaviour dates back to Sherwood (1993), Dormieux et al. (1995) and Heidug and Wong (1996). Sherwood (1993) and Heidug and Wong (1996) restricted their analysis to the case of solutions containing an uncharged solute, while

DRAFT

Dormieux et al. (1995) considered only mechanical constitutive equations for clays in equilibrium with a solution containing a single salt in solution.

The phenomenological approach is here developed with reference to a solution containing N ion species, and accounting for both mechanical and transport constitutive equations. The main simplifying assumptions adopted in the analysis are:

1. unidimensional geometry (spatial coordinate, x), representing the reference problem of Fig. 1;
2. infinitesimal strains of the solid skeleton;
3. saturated porous medium (the voids are filled with an electrolyte solution);
4. incompressible solid and liquid phase;
5. infinitely diluted electrolyte solution;
6. complete dissociation of the salts in the solution;
7. absence of chemical reactions.

A unidimensional geometry assumption means that the only nonzero fluxes (i.e. mass flux, momentum flux, energy flux, entropy flux.) exist in the x direction. As in the scheme of Fig. 1, the soil is represented by a layer that can only undergo vertical strains, which are also volumetric strains. The vertical displacements are assumed to be sufficiently small in order to make the hypothesis of infinitesimal strains reasonable.

Assumptions 1-4 are analogous to those adopted to derive Terzaghi's consolidation equation, which is very familiar to geotechnical engineers. These assumptions have been proved to be acceptable for most applications that are encountered in geotechnical engineering. However, it should be stressed that in some cases they cannot be considered reasonable: for instance, in the case of very compressible clay soils, characterized by a water content close to the Atterberg liquid limit, the expected strains cannot be assumed infinitesimal and finite strains

DRAFT

have to be accounted for; similarly, when clay soils undergo a desiccation process, the water saturation condition is generally not verified and air can enter the soil pores.

Assumptions 5-7 are relative to the electrolyte solution that permeates the soil. The assumption of ideal, i.e. infinitely diluted, solution is generally considered acceptable when dealing with natural soil water or landfill leachate, due to the very low ion concentrations that are normally encountered (Bear, 1972; Freeze and Cherry, 1979). However, in some cases, relatively high ion concentrations can be found, as in the case of the proximity of sea water, therefore such an assumption cannot be adopted and corrective terms need to be introduced, as illustrated in Appendix B. In the present work, partial salt dissociation and chemical reactions are not taken into account, but they could be introduced in the analysis by considering the presence of neutral solutes and by adding a source/sink term to the mass balance equations.

In the proposed approach, the transport constitutive equations are developed starting from the expression of the dissipation function, Φ, whose derivation from the mass, momentum, energy and entropy balances is reported in Appendix A. The mechanical constitutive equations are restricted to the assumption of elastic behaviour of the solid skeleton, and are derived from the expression of the Legendre transform of the Helmholtz free energy of the solid skeleton, with reference to the initial or undeformed volume, $\mathfrak{I}_V^{sk\prime}$. The derivation of the expression of $\mathfrak{I}_V^{sk\prime}$ is reported in Appendix A.

DRAFT

MASS BALANCES

In the approach of classical thermodynamics of irreversible processes, the equations governing the transport of the fluid components through the porous media are the mass balances of these components. If the fluid moving through the porous medium is a diluted electrolyte solution, the mass balance equations for the unidimensional case, under the assumption of small strains of the porous medium, can be expressed as follows (Gibson et al., 1967; Peters and Smith, 2002; Coussy, 2004):

$$\frac{\partial \zeta}{\partial t} = -\frac{\partial q}{\partial x} \tag{1a}$$

$$\frac{1}{1+e_0}\frac{\partial (e \cdot \bar{c}_i)}{\partial t} = -\frac{\partial J_i}{\partial x} \qquad \text{for } i = 1, 2, \ldots, N \tag{1b}$$

where:

N = number of ions contained in the pore solution (-);

ζ = increment of fluid content (-);

e = current void index, defined as the ratio between the void volume and the solid volume (-);

e_0 = void index corresponding to the initial or undeformed state (-).

$\bar{c}_i$ = i-th ion concentration, referring to the pore solution ($mol \cdot m^{-3}$);

q = Darcy's velocity or volumetric flux of the electrolyte solution relative to the solid skeleton, which is assumed approximately equal to the volumetric flux of water, due to the assumption of a diluted solution ($m \cdot s^{-1}$);

J_i = i-th ion molar flux ($mol \cdot m^{-2} \cdot s^{-1}$) relative to the solid skeleton.

The increment of fluid content, ζ, for a saturated porous medium with incompressible constituents, can be related to the current void index, e, as follows:

DRAFT

$$d\zeta = \frac{de}{1+e_0} \tag{2}$$

The following relation between the increment of fluid content, ζ, and the strain, ε (-), exists:

$$d\zeta = -d\varepsilon \tag{3}$$

where the compression strain has been assumed positive.

The volumetric flux of the solution relative to the solid skeleton is defined as follows:

$$q = n \cdot (v_w - v_{sk}) \tag{4}$$

where:

n = soil porosity (-);

v_w = water velocity ($m \cdot s^{-1}$);

v_{sk} = solid skeleton velocity ($m \cdot s^{-1}$).

The flux of i-th ion relative to the solid skeleton is defined as follows:

$$J_i = n \cdot \bar{c}_i \cdot (v_i - v_{sk}) \qquad \text{for } i = 1, 2, \dots, N \tag{5}$$

where:

v_i = velocity of i-th ion ($m \cdot s^{-1}$).

DRAFT

Given mass balances (1) and (2), the constitutive problem is that of finding suitable relations between ζ, $\frac{e \cdot \bar{c}_i}{1+e_0}$, q and J_i with the virtual variables c_i, u and φ.

DRAFT

TRANSPORT EQUATIONS

For the fluxes q and J_i, reference is made to the expression of the dissipation function, Φ ($J \cdot s^{-1} \cdot m^{-3}$), defined as the rate of entropy production multiplied by the absolute temperature, which is derived in Appendix A:

$$\Phi = -q \cdot \left(\frac{\partial u}{\partial x} - \frac{\partial \Pi}{\partial x} - \rho_w g \right) - \sum_{i=1}^{N} J_i \cdot \left(\frac{\partial \mu_i^{ec}}{\partial x} \right) \geq 0 \qquad (6)$$

where:

$\Pi = R \cdot T \cdot \sum_{i=1}^{N} c_i$ = osmotic pressure of the virtual solution ($N \cdot m^{-2}$);

R = universal gas constant (= 8.314 $J \cdot mol^{-1} \cdot K^{-1}$);

T = absolute pressure (K);

ρ_w = water density (= $1 \cdot 10^3$ $kg \cdot m^{-3}$);

g = gravitational acceleration ($\cong$ 9.81 $m \cdot s^{-2}$);

$d\mu_i^{ec} = (d\mu_i)_T + z_i F \cdot d\varphi$ = differential of the electro-chemical potential of i-th ion ($J \cdot mol^{-1}$);

F = Faraday's constant (= 96,485 $C \cdot mol^{-1}$);

z_i = electro-chemical valence of the i-th ion (-);

$(d\mu_i)_T = \frac{R \cdot T}{c_i} dc_i$ = differential of the chemical potential of i-th ion at constant temperature ($J \cdot mol^{-1}$).

When deriving Eq. 6, the x coordinate has been taken in the direction of gravity.

The expression of the dissipation function Φ is generally interpreted by assuming that the terms in brackets represent the thermodynamic forces acting on the system, and producing the

DRAFT

thermodynamics fluxes q and J_i. The constitutive assumption is that the fluxes depend on these thermodynamic forces, through the simplest acceptable relationship , i.e. the linear one:

$$q = -\ell_{ww}\left(\frac{\partial u}{\partial x} - \frac{\partial \Pi}{\partial x} - \rho_w g\right) - \sum_{i=1}^{N} \ell_{wi} \frac{\partial \mu_i^{ec}}{\partial x} \tag{7a}$$

$$J_i = -\ell_{iw}\left(\frac{\partial u}{\partial x} - \frac{\partial \Pi}{\partial x} - \rho_w g\right) - \sum_{j=1}^{N} \ell_{ij} \frac{\partial \mu_j^{ec}}{\partial x} \qquad \text{for } i = 1, 2, \ldots, N \tag{7b}$$

where ℓ_{ab} represents the phenomenological coefficient that relates flux "a" to thermodynamic force "b".

Using statistical mechanics methods, Onsager (1931a,b) was able to show that the matrix of phenomenological coefficients is symmetric, or that:

$$\ell_{ab} = \ell_{ba} \text{ for } a, b = w, 1, 2, \ldots, N \text{ when } a \neq b. \tag{8}$$

The Onsager reciprocal relations given in Eqs. 8 were questioned by Truesdell (1984a,b), who criticized their theoretical derivation and application to diffusion, viscosity and heat transport problems. However, Dominijanni and Manassero (2010 and 2011) have shown that these relations can be verified for a physical model, derived from the assumption that the macroscopic chemical potentials of fluid components between the real and the virtual solution are equal. For this model, the symmetry of the matrix of phenomenological coefficients is a consequence of the hypothesis of infinite dilution of the electrolyte solution and the resulting binary drag between the mixture components. Within the scope of the phenomenological approach, it is also very important to point out that the Onsager relations were verified experimentally by Letey and Kemper (1969) on clay soils. Considering such experimental

DRAFT

results, Eqs. 8 can be considered as a phenomenological assumption, sustained by experimental verification, and not as the result of a theorem.

An alternative form of the phenomenological equations, which is particularly suitable for the experimental determination of phenomenological coefficients, is the following:

$$q = -\ell_{ww}\left[\left(\frac{\partial u}{\partial x} - \frac{\partial \Pi}{\partial x} - \rho_w g\right) + \sum_{i=1}^{N}(1-\omega_i)\cdot c_i \cdot \frac{\partial \mu_i^{ec}}{\partial x}\right] \tag{9a}$$

$$J_i = (1-\omega_i)\cdot c_i \cdot q - \sum_{j=1}^{N} \tilde{\ell}_{ij} \frac{\partial \mu_j^{ec}}{\partial x} \qquad \text{for } i = 1, 2, \ldots, N \tag{9b}$$

where

$$\omega_i = 1 - \frac{1}{c_i}\frac{\ell_{iw}}{\ell_{ww}} \tag{10}$$

$$\tilde{\ell}_{ij} = \ell_{ij} - \frac{\ell_{iw}\ell_{jw}}{\ell_{ww}}\,. \tag{11}$$

When the analysis is devoted to evaluating the migration of an electrolyte solution through a bentonite barrier, the condition in which no electrical current exists across the soil needs to be taken into account:

$$I_e = F\cdot\left(\sum_{i=1}^{N} z_i J_i\right) = 0 \tag{12}$$

where I_e is the electric current density.

DRAFT

This condition is usually relevant for engineered containment applications, in that most containment systems do not involve the application of an electrical current across the soil barrier (Malusis and Shackelford, 2002). The application of this equation, together with Eqs. 7 or 9, allows the electric potential gradient to be eliminated from the transport equations, which result to only have the virtual hydraulic pressure, u, and the virtual ion concentrations, c_i, as variables.

The most relevant case of practical interest is when the pore solution contains a single salt:

$$(\text{Counter}-\text{ion})_{z_1}^{\nu_1}(\text{Co}-\text{ion})_{z_2}^{\nu_2}$$

consisting of a counter-ion (charge polarity opposite that of the solid skeleton charge) and a co-ion (same charge polarity as the solid skeleton); (ν_1, z_1) and (ν_2, z_2) are the stoichiometric coefficient and the electrochemical valence of the counter-ion (index 1) and the co-ion (index 2), respectively. Montmorillonite particles have a negative net electric charge: as a result, the counter-ions are the cations (positive charged ion molecules) and the co-ions are the anions (negative charged ion molecules).

The salt in solution is considered to be completely dissociated with the following stoichiometric reaction:

$$(\text{Counter}-\text{ion})_{z_1}^{\nu_1}(\text{Co}-\text{ion})_{z_2}^{\nu_2} \rightarrow \nu_1(\text{Counter}-\text{ion})^{z_1} + \nu_2(\text{Co}-\text{ion})^{z_2}.$$

If c_1 and c_2 represent the concentration of the counter-ion and co-ion, respectively, the salt concentration, c_s, can be defined as follows:

DRAFT

$$c_s = \frac{c_1}{\nu_1} = \frac{c_2}{\nu_2}. \tag{13}$$

In this case, the dissipation function can be expressed as follows:

$$\Phi = -q \cdot \left(\frac{\partial u}{\partial x} - \frac{\partial \Pi}{\partial x} - \rho_w g \right) - J_1 \cdot \left(\frac{\partial \mu_1^{ec}}{\partial x} \right) - J_2 \cdot \left(\frac{\partial \mu_2^{ec}}{\partial x} \right) \geq 0 \tag{14}$$

Using the electro-chemical potential and electric current definition, Eq. 13 can be expressed as follows:

$$\Phi = -q \cdot \left(\frac{\partial u}{\partial x} - \rho_w g \right) + q \cdot \left(\frac{\partial \Pi}{\partial x} \right) - J_1 \cdot \left(\frac{\partial \mu_1}{\partial x} \right)_T - J_2 \cdot \left(\frac{\partial \mu_2}{\partial x} \right)_T - I_e \cdot \left(\frac{\partial \varphi}{\partial x} \right) \geq 0 \tag{15}$$

Under the condition of no electric current (i.e. $I_e = 0$), the last term in Eq. 15 is dropped, and the ionic fluxes are related as follows:

$$J_s = \frac{J_1}{\nu_1} = \frac{J_2}{\nu_2} \tag{16}$$

where:

J_s = mass flux of the salt ($mol \cdot m^{-2} \cdot s^{-1}$).

Then, using the following definition of the chemical potential gradient of the salt:

$$\left(\frac{\partial \mu_s}{\partial x} \right)_T = \nu_1 \left(\frac{\partial \mu_1}{\partial x} \right)_T + \nu_2 \left(\frac{\partial \mu_2}{\partial x} \right)_T \tag{17}$$

DRAFT

and observing that

$$\frac{\partial \Pi}{\partial x} = c_s \left(\frac{\partial \mu_s}{\partial x} \right)_T \tag{18}$$

the dissipation function can be written in the following form:

$$\Phi = -q \cdot \left(\frac{\partial u}{\partial x} - \rho_w g \right) - J_s^d \cdot \left(\frac{\partial \mu_s}{\partial x} \right)_T \geq 0 \tag{19}$$

where

$J_s^d = J_s - qc_s$ = salt mass flux relative to the solvent ($mol \cdot m^{-2} \cdot s^{-1}$).

On the basis of such an expression of the dissipation function, the phenomenological equations can be formulated as follows:

$$q = -\alpha_{ww} \left(\frac{\partial u}{\partial x} - \rho_w g \right) - \alpha_{ws} \left(\frac{\partial \mu_s}{\partial x} \right)_T \tag{20a}$$

$$J_s^d = -\alpha_{sw} \left(\frac{\partial u}{\partial x} - \rho_w g \right) - \alpha_{ss} \left(\frac{\partial \mu_s}{\partial x} \right)_T . \tag{20b}$$

or in the following alternative way, which is more suitable for an experimental determination of phenomenological coefficients:

$$q = -\alpha_{ww} \left(\frac{\partial u}{\partial x} - \rho_w g - \omega \frac{\partial \Pi}{\partial x} \right) \tag{21a}$$

DRAFT

$$J_s = (1-\omega)\cdot q \cdot c_s - P_s \cdot \frac{\partial c_s}{\partial x} \qquad (21b)$$

where:

$\omega = -\frac{\alpha_{ws}}{\alpha_{ww} c_s}$ = reflection coefficient or chemico-osmotic efficiency coefficient, which is also frequently indicated with the symbol σ in biological and chemical literature (-);

$P_s = \left(\alpha_{ss} - \frac{\alpha_{sw}^2}{\alpha_{ww}}\right)\frac{RT(\nu_1+\nu_2)}{c_s}$ = solute permeability ($m^2 \cdot s^{-1}$).

It should be pointed out that the denomination of "chemico-osmotic efficiency coefficient" for the parameter ω can generate confusion, since such a parameter is not always expected to be between 0 and 1. For instance, Kemper and Quirk (1972) measured negative values of ω on clay samples. The thermodynamic condition $\Phi \geq 0$ expressed by Eq. 19 implies the following restrictions on the phenomenological coefficients:

$$\alpha_{ww} \geq 0 \qquad (22a)$$

$$\alpha_{ss} \geq 0 \qquad (22b)$$

$$\alpha_{ww} \cdot \alpha_{ss} \geq \alpha_{sw}^2 \qquad (22c)$$

$$P_s \geq 0, \qquad (22d)$$

while coefficient ω can assume any value. For this reason, the denomination of "reflection coefficient" for ω is preferred to that of "chemico-osmotic efficiency coefficient".

The coefficient α_{ww} can be measured, under steady state conditions, using traditional permeameters. Malusis et al. (2001) developed a new testing apparatus to determine ω and P_s. This apparatus is able to impose the condition of no-volumetric flux (q = 0) through a soil

DRAFT

sample in contact with two external solutions, maintained at constant salt concentrations, so that the global or averaged values of the coefficients can be measured. The global values of ω and P_s are defined as follows (Auclair et al., 2002):

$$\omega_g = \frac{1}{\Delta c_s} \int_{c_s'}^{c_s''} \omega \cdot dc_s \tag{23a}$$

$$P_{sg} = \frac{1}{\Delta c_s} \int_{c_s'}^{c_s''} P_s \cdot dc_s \tag{23b}$$

where c_s' and c_s'' represent the salt concentration at the boundaries of the clay sample and $\Delta c_s = c_s' - c_s''$ is their difference. These coefficients can be determined by means of the following relations under steady state conditions:

$$\omega_g = \left(\frac{\Delta u}{\Delta \Pi} \right)_{q=0} \tag{24a}$$

$$P_{sg} = L \left(\frac{J_s}{\Delta c_s} \right)_{q=0} \tag{24b}$$

where $\Delta u = u' - u''$ and $\Delta \Pi = \Pi' - \Pi''$ represent the difference between the hydraulic pressure and the osmotic pressure at the boundaries of the clay sample, respectively, and L (m) is the length of the sample.

At this point, a comparison with the more common transport equations of the advective-diffusive transport theory can be useful. The volumetric flux q is usually evaluated through the Darcy equation (Bear, 1972; Freeze and Cherry, 1979):

DRAFT

$$q = -\frac{k}{\rho_w g}\left(\frac{\partial u}{\partial x} - \rho_w g\right) \tag{25a}$$

where:

k = hydraulic conductivity ($m \cdot s^{-1}$).

The solute transport is usually governed by the advective-diffusive equation (Shackelford, 1993):

$$J_s = q \cdot c_s - n \cdot D_s^* \cdot \frac{\partial c_s}{\partial x} \tag{25b}$$

where:

$D_s^* = \tau_m \cdot D_{s,0}$ = effective diffusion coefficient of the salt ($m^2 \cdot s^{-1}$);

τ_m = non-dimensional matrix tortuosity factor (<1);

$D_{s,0}$ = free-solution diffusion coefficient of the salt.

The coefficient τ_m accounts for the tortuous nature of the actual diffusive pathways through the porous medium due to the geometry of the interconnected pores. The free-solution diffusion coefficient of the salt, $D_{s,0}$, is given by (Robinson and Stokes, 1959; Shackelford, 1989):

$$D_{s,0} = \frac{(\nu_1 + \nu_2) D_{1,0} D_{2,0}}{\nu_1 D_{2,0} + \nu_2 D_{1,0}} = \frac{(|z_1| + |z_2|) D_{1,0} D_{2,0}}{|z_1| D_{1,0} + |z_2| D_{2,0}} \tag{26}$$

where $D_{1,0}$ and $D_{2,0}$ are the free-solution diffusion coefficients of the counter-ion and of the co-ion, respectively.

DRAFT

A comparison of Eqs. 25 with Eqs. 20 and 21 shows that there is a correspondence when $\alpha_{sw} = \alpha_{ws} = 0$ (or $\omega = 0$). In this particular case, the following correspondence between the phenomenological parameters and the more common transport coefficients can be found:

$$\alpha_{ww} = \frac{k}{\gamma_w} \tag{27a}$$

$$\alpha_{ss} = n \cdot D_s^* \frac{c_s}{R \cdot T \cdot (\nu_1 + \nu_2)} \tag{27b}$$

$$P_s = n \cdot D_s^* \tag{27c}$$

It is relevant to point out that Eqs. 27 only refer to the particular case for which $\alpha_{sw} = \alpha_{ws} = 0$ (or $\omega = 0$). In this case, the transport Eqs. 21 are not coupled and the classical advective-diffusive transport theory is restored.

Eq. 27b has in particular generated some confusion, since it has been assumed to also be valid when $\alpha_{sw} = \alpha_{ws} \neq 0$ (or $\omega \neq 0$) (Yeung and Mitchell, 1993; Mitchell, 1993) and has been considered as an identification of the physical meaning of α_{ss}. In reality, the physical identification of α_{ss} needs an adequate physical model that accounts for the interaction between montmorillonite lamellae and the ions in a pore solution and, when $\alpha_{sw} = \alpha_{ws} \neq 0$ (or $\omega \neq 0$), the relation with the effective diffusion coefficient of the salt is not so straightforward.

When $\alpha_{sw} = \alpha_{ws} \neq 0$ (or $\omega \neq 0$), the porous medium is said to be semipermeable or permiselective, due to the fact that the transport resistance exerted by the medium differs for the components of the liquid phase.

A special condition that can be reached by a semipermeable porous medium is that in which the salt flux is completely hindered, i.e. $J_s = 0$. Looking at Eq. 21b, this condition is met when $\omega = 1$ and $P_s = 0$. In this special case, the semi-permeable porous medium is said to be "ideal"

DRAFT

or "perfect", because it is able to completely hinder the passage of the salt, and act as a perfectly efficient barrier.

Based on such considerations, it can be concluded that the coupled flux theory based on the phenomenological approach of the thermodynamics of irreversible processes includes the more common advective-diffusive transport theory as a particular case.

DRAFT

PORO-ELASTIC CONSTITUTIVE EQUATIONS

If elastic behaviour is assumed for the porous medium, the constitutive equation of ζ and $(e \cdot \bar{c}_i)/(1+e_0)$ can be inferred from the expression of function $\Im_V^{sk}{}'$, which represents the Legendre transform of the Helmholtz free energy of the solid skeleton, referring to the initial or undeformed volume, and whose derivation, under the assumption of infinitesimal strains, is reported in Appendix A:

$$d\Im_V^{sk}{}' = \varepsilon \cdot [d\sigma - (du - d\Pi)] + \sum_{i=1}^{N} \frac{e \cdot \bar{c}_i}{1+e_0} \cdot (d\mu_i)_T \,. \tag{28}$$

The function $\Im_V^{sk}{}'$ can be considered to depend on the variables $[\sigma - (u - \Pi)]$ and $(\mu_i)_T$, therefore the simplest constitutive equations that can be inferred are:

$$d\varepsilon = \beta_{vv} \cdot [d\sigma - (du - d\Pi)] + \sum_{i=1}^{N} \beta_{vi} \cdot (d\mu_i)_T \tag{29a}$$

$$\frac{d(e \cdot \bar{c}_i)}{1+e_0} = \beta_{iv} [d\sigma - (du - d\Pi)] + \sum_{j=1}^{N} \beta_{ij} \cdot (d\mu_j)_T \qquad \text{for } i = 1,2,...,N \tag{29b}$$

At this point, it could be useful to point out that, in the absence of a partition effect for the solute in the porous medium, i.e. when $\bar{c}_i = c_i$, the expression of $\Im_V^{sk}{}'$, using the following identity $d\Pi = \sum_{i=1}^{N} c_i (d\mu_i)_T$, is reduced to the following expression (see Appendix A):

$$d\Im_V^{sk}{}' = \varepsilon \cdot (d\sigma - du) \,. \tag{30}$$

DRAFT

Such an expression of $\Im_V^{sk}{}'$ can be considered as a theoretical justification for the Terzaghi's effective stress definition $d\sigma' = d\sigma - du$, and the use of an elastic relationship of the type:

$$d\varepsilon = \beta \cdot d\sigma'. \tag{31}$$

It should be stressed that the classical results of soil mechanics are restored when there is no ion partition effect.

A case of practical interest is that in which a single salt, assumed completely dissociated, is present in the pore solution. In such a case, Eq. 28 can be written as follows:

$$d\Im_V^{sk}{}' = \varepsilon \cdot \left[d\sigma - (du - d\Pi)\right] + \left[\frac{e \cdot (\bar{c}_1 + \bar{c}_2)}{1 + e_0}\right] \cdot \frac{1}{\nu_1 + \nu_2} (d\mu_s)_T. \tag{32}$$

Such an expression of $\Im_V^{sk}{}'$ suggests the following constitutive equations:

$$d\varepsilon = \beta_{vv} \cdot \left[d\sigma - (du - d\Pi)\right] + \beta_{vs} \cdot (d\mu_s)_T \tag{33a}$$

$$\frac{d\left[e \cdot (\bar{c}_1 + \bar{c}_2)\right]}{(\nu_1 + \nu_2)(1 + e_0)} = \beta_{sv}\left[d\sigma - (du - d\Pi)\right] + \beta_{ss} \cdot (d\mu_s)_T \tag{33b}$$

Symmetry of the coefficients, i.e. $\beta_{vs} = \beta_{sv}$, can be demonstrated by considering $\Im_V^{sk}{}'$ as a continuous function of the variables $\alpha = \left[\sigma - (u - \Pi)\right]$ and $\beta = (\mu_s)_T$. Therefore,

$$\frac{\partial \Im_V^{sk}{}'}{\partial \alpha} = \varepsilon \tag{34a}$$

DRAFT

$$\frac{\partial \mathfrak{I}_V^{sk'}}{\partial \beta} = \frac{e \cdot (\bar{c}_1 + \bar{c}_2)}{(\nu_1 + \nu_2)(1 + e_0)} = \gamma \,. \tag{34b}$$

The mixed partial derivatives $\frac{\partial^2 \mathfrak{I}_V^{sk'}}{\partial \alpha \partial \beta} = \frac{\partial^2 \mathfrak{I}_V^{sk'}}{\partial \beta \partial \alpha}$ must be equal, hence

$$\frac{\partial \varepsilon}{\partial \beta} = \frac{\partial \gamma}{\partial \alpha} \tag{35}$$

which, for Eqs. 33, implies $\beta_{vs} = \beta_{sv}$.

In conclusion, it is of interest to observe that constitutive Eq. 33a can be compared with the equation proposed on an empirical basis by Barbour and Fredlund (1989) and which has been used by various authors (e.g. Kaczmarek and Hueckel, 1998 and Peters and Smith, 2004):

$$d\varepsilon = m_v \cdot (d\sigma - du) + m_\pi \cdot d\Pi \,. \tag{36}$$

where m_v and m_π are phenomenological parameters.

Correspondence between Eq. 33a and Eq. 36 can be obtained taking

$$m_v = \beta_{vv} \tag{37a}$$

$$m_\pi = \beta_{vv} + \frac{\beta_{vs}}{c_s} \tag{37b}$$

and observing that $(d\mu_s)_T = \frac{d\Pi}{c_s}$.

DRAFT

Another comparison of interest is that of the constitutive equations proposed by Dormieux et al. (1995) and, successively developed by Dormieux et al. (2003) and Coussy (2004). With reference to Coussy (2004) and using the notation of this paper, the constitutive equations for a swelling clay soil, in equilibrium with a solution containing a single salt assumed completely dissociated, can be expressed as follows:

$$d\sigma - (du - d\Pi) = K \cdot d\varepsilon + b_{\ell} d\Pi \tag{38a}$$

$$\frac{1}{1+e_0} d\left[\frac{e}{A}\right] = -b_{\ell} \cdot d\varepsilon + \frac{1}{N} \cdot d\Pi \tag{38b}$$

where

K = skeleton bulk modulus;

b_{ℓ} = Biot's coefficient;

A = chemical activity of the salt in solution;

N = poro-elastic coefficient of the salt.

The activity coefficient accounts for the salt partition effect in the porous medium and is defined as follows:

$$A = \frac{c_s(\nu_1 + \nu_2)}{\bar{c}_1 + \bar{c}_2}. \tag{39}$$

It is necessary to point out that, using such a definition of A, the partition effect is governed by the cation attraction, therefore smaller values of A than 1 are expected in the presence of a partition effect, while A = 1 is the condition that corresponds to the absence of a partition effect within the porous medium.

DRAFT

In order to compare the Coussy (2004) constitutive equations with those proposed in this paper, the following identity can be useful:

$$\frac{1}{1+e_0}d\left(\frac{e}{A}\right)=\frac{d\left[e\cdot(\bar{c}_1+\bar{c}_2)\right]}{(1+e_0)\cdot(\nu_1+\nu_2)\cdot c_s}-\frac{e\cdot(\bar{c}_1+\bar{c}_2)\cdot d\Pi}{(1+e_0)\cdot RT\cdot(\nu_1+\nu_2)^2\cdot c_s^2} \tag{40}$$

Using such an identity, the Coussy (2004) constitutive equations can be written as follows:

$$d\sigma-(du-d\Pi)=K\cdot d\varepsilon+b_\ell d\Pi \tag{41a}$$

$$\frac{d\left[e\cdot(\bar{c}_1+\bar{c}_2)\right]}{(1+e_0)\cdot(\nu_1+\nu_2)\cdot c_s}=-b_\ell\cdot d\varepsilon+\left(\frac{1}{N}+\frac{e\cdot(\bar{c}_1+\bar{c}_2)}{(1+e_0)\cdot RT\cdot(\nu_1+\nu_2)^2\cdot c_s^2}\right)\cdot d\Pi \tag{41b}$$

In order to recast Eqs.33 in the same form as the Coussy (2004) constitutive equations, it is sufficient to derive $\left[d\sigma-(du-d\Pi)\right]$ from Eq.33a and to substitute the obtained relation in Eq.33b, divided by c_s, so that:

$$d\sigma-(du-d\Pi)=\frac{1}{\beta_{vv}}\cdot d\varepsilon-\left(\frac{\beta_{vs}}{\beta_{vv}\cdot c_s}\right)d\Pi \tag{42a}$$

$$\frac{d\left[e\cdot(\bar{c}_1+\bar{c}_2)\right]}{(1+e_0)\cdot(\nu_1+\nu_2)\cdot c_s}=\frac{\beta_{sv}}{\beta_{vv}\cdot c_s}\cdot d\varepsilon+\left(\frac{\beta_{ss}}{c_s^2}-\frac{\beta_{vs}^2}{\beta_{vv}\cdot c_s^2}\right)\cdot d\Pi \tag{42b}$$

Comparing Eqs. 41 and Eqs. 42, the following relations can be found between the phenomenological parameters of this paper and those of Coussy (2004):

$$K=\frac{1}{\beta_{vv}} \tag{43a}$$

DRAFT

$$b_\ell = -\frac{\beta_{vs}}{\beta_{vv} \cdot c_s} \tag{43b}$$

$$N = \frac{1}{\frac{\beta_{ss}}{c_s^2} - \frac{\beta_{vs}^2}{\beta_{vv} \cdot c_s^2} - \frac{e \cdot (\bar{c}_1 + \bar{c}_2)}{(1+e_0) \cdot RT \cdot (\nu_1 + \nu_2)^2 \cdot c_s^2}} \tag{43c}$$

It is interesting to note that Eq. 33a can also be expressed in the following form:

$$d\sigma - du - du_{sw} = M \cdot d\varepsilon \tag{44}$$

where $M = 1/\beta_{vv} = K$ is the unidimensional elastic modulus of the porous medium (in geotechnical literature, the symbol M is used more frequently than Coussy's symbol K) and du_{sw} represents the swelling pressure, which is given by:

$$du_{sw} = -\varpi \cdot d\Pi \tag{45}$$

where $\varpi = 1 + \frac{\beta_{vs}}{\beta_{vv} \cdot c_s} = 1 - b_\ell$ is the swelling coefficient.

From experimental observations, it is known that the swelling pressure tends to zero when $c_s \to \infty$, therefore u_{sw} can be obtained as follows:

$$u_{sw} = \int_{\Pi}^{\infty} \varpi \cdot d\Pi \,. \tag{46}$$

DRAFT

Eq. 44 represents a relevant theoretical result, since it allows the effective stress principle to be reformulated and extended to charged soils. The effective stresses, in fact, can be identified with the term on the left hand side of Eq. 44, i.e.

$$d\sigma' = d\sigma - du - du_{sw} \tag{47}$$

Terzaghi's definition of effective stress, as already stated, corresponds to the particular case for which $du_{sw} = 0$, i.e. $\beta_{vs} = 0$. Therzaghi's poro-elastic theory for non-swelling soils is therefore restored as a special case of the more general theory developed for swelling clays.

DRAFT

CONCLUSIONS

The final set of equations governing the consolidation and transport problem of a clay barrier can be formulated by inserting the mechanical and transport constitutive equations (i.e. Eqs. 7 and 29) into the mass balances (Eqs. 1). Assuming that the total stress is maintained constant in time, i.e. $\partial\sigma/\partial t = 0$, the resulting set of equations is given by:

$$\beta_{vv}\frac{\partial(u-\Pi)}{\partial t} - \sum_{i=1}^{N}\beta_{vi}\left(\frac{\partial \mu_i}{\partial t}\right)_T = \frac{\partial}{\partial x}\left\{\ell_{ww}\left(\frac{\partial(u-\Pi)}{\partial x} - \rho_w g\right) + \sum_{i=1}^{N}\ell_{wi}\left[\left(\frac{\partial \mu_i}{\partial x}\right)_T + z_i F\frac{\partial \varphi}{\partial x}\right]\right\} \quad (48a)$$

$$\beta_{iv}\frac{\partial(u-\Pi)}{\partial t} - \sum_{j=1}^{N}\beta_{ij}\left(\frac{\partial \mu_j}{\partial t}\right)_T = \frac{\partial}{\partial x}\left\{\ell_{iw}\left(\frac{\partial(u-\Pi)}{\partial x} - \rho_w g\right) + \sum_{j=1}^{N}\ell_{ij}\left[\left(\frac{\partial \mu_j}{\partial x}\right)_T + z_i F\frac{\partial \varphi}{\partial x}\right]\right\} \quad (48b)$$

$$i = 1,2,\ldots,N$$

Eqs. 48 are a set of N+1 equations for the N+2 variables c_i, u and φ. The gradient of the electric potential φ can be eliminated from Eqs. 48, using the condition of nil electric current, i.e. $I_e = F\cdot\sum_{i=1}^{N} z_i J_i = 0$, and reducing the number of variables to N. If the condition of electroneutrality of the virtual solution, i.e. $\sum_{i=1}^{N} z_i c_i = 0$, is accounted for, one variable can be eliminated, and the number of equations is thus reduced from N+1 to N.

The resulting set of equations can be solved together with the boundary conditions, expressed as function of c_i and u and of their time and space first derivatives.

The phenomenological approach, using the formalism of the thermodynamics of irreversible processes, allows a consistent formulation to be made of the consolidation and transport problem that accounts for swelling and osmotic effects. This result is obtained without any specification of the physical and chemical phenomena that occur at the pore scale and determine such effects at the macroscopic scale of observation. Thermodynamics

DRAFT

considerations define the number of phenomenological coefficients necessary for the analysis and restrict the values that they can assume. However, on the basis of the phenomenological approach, all the coefficients should be measured through macroscopic experimental tests. The resulting number of tests necessary for the characterization of a single clay is extremely high, considering that all the coefficient are unknown functions of the state variables c_i and u. From a practical point of view, it could be unfeasible to carry out such a high number of tests. For this reason, the phenomenological approach should be opportunely combined with a physical one, which, starting from the identification of the interactions that take place at the pore scale between the montmorillonite lamellae and the liquid phase, allows the phenomenological coefficient to be related to a limited number of physical and chemical properties of the clay soil. In this way, a restricted number of tests needs to be carried out in order to obtain necessary data for the evaluation of the behaviour of clay in field applications.

DRAFT

APPENDIX A

A derivation of Eqs. 1, 6 and 28 of the main text is reported in this Appendix. Such a derivation is based on the formalism of the thermodynamics of irreversible processes, which has been developed in more detail in De Groot and Mazur (1962), Katchalsky and Curran (1965), Haase (1990), Coussy (1995 and 2004) and Revil (2007).

Mass balance equations

The mass balance equations for all the components of the system, i.e. the solid skeleton (index sk), water (index w) and ion species (index i = 1, 2, … , N), need to be considered.

In the absence of chemical reactions, the generic mass balance for the r-th component of the porous medium (r = sk, w, 1, 2, … , N), which is assumed completely saturated by the liquid phase, can be expressed as:

$$\frac{\partial(n \cdot \bar{c}_r)}{\partial t} = -\frac{\partial(n \cdot \bar{c}_r \cdot v_r)}{\partial x}. \tag{A1}$$

where $\bar{c}_r$ represents the molar concentration relative to the pore volume.

For the water component, the following relationship holds:

$$\bar{c}_w = c_w = \frac{\rho_w}{M_w} \tag{A2}$$

where ρ_w and M_w are the water density and molar mass, respectively.

For the electric charges of the solid skeleton, the molar concentration per unit volume of pore volume can be expressed as follows:

DRAFT

$$\bar{c}_{sk} = \frac{\bar{c}_{sk,0}}{e} = \frac{\bar{c}_{sk,0} \cdot (1-n)}{n} \tag{A3}$$

where $\bar{c}_{sk,0}$ represents the solid molar mass per unit volume of the solid phase.

Using the relationships A2 and A3 and assuming that ρ_w and $\bar{c}_{sk,0}$ are constant, the mass balances for the porous medium can be expressed in terms of spatial coordinates as follows:

water: $$\frac{\partial n}{\partial t} = -\frac{\partial (n \cdot v_w)}{\partial x} \tag{A4a}$$

ions: $$\frac{\partial (n \cdot \bar{c}_i)}{\partial t} = -\frac{\partial I_i}{\partial x} \tag{A4b}$$

solid skeleton $$\frac{\partial (1-n)}{\partial t} = -\frac{\partial [(1-n) \cdot v_{sk}]}{\partial x} \tag{A4c}$$

where:

v_w = water velocity ($m \cdot s^{-1}$);

v_{sk} = solid skeleton velocity ($m \cdot s^{-1}$);

$I_i = n\bar{c}_i v_i$ = absolute flux of the i-th ion ($mol \cdot m^{-2} \cdot s^{-1}$);

v_i = velocity of the i-th ion ($m \cdot s^{-1}$).

The mass balances given by Eqs. A4 can also be expressed in terms of material coordinates, assuming that the coordinate system deforms with the solid skeleton.

The relationship between the spatial and material coordinates is given by (Peters and Smith, 2002):

$$x(a, \tau) = \xi(a, \tau) \tag{A5a}$$

DRAFT

$$t(a,\tau) = \tau \tag{A5b}$$

where x and t are the spatial and temporal coordinates in the spatial coordinate system; a and τ are the spatial and temporal coordinates in the material coordinate system; ξ is an unknown function that describes the relationship between x and the material coordinates a and τ.

The chain rule of differentiation can be used to derive the transformation rules between the spatial and material coordinate systems:

$$\frac{\partial}{\partial a} = J \cdot \frac{\partial}{\partial x} \tag{A6a}$$

$$\frac{\partial}{\partial \tau} = \frac{\partial}{\partial t} + v_{sk} \frac{\partial}{\partial x} \tag{A6b}$$

where $v_{sk} = \frac{\partial \xi}{\partial \tau}$ and $J = \frac{\partial \xi}{\partial a} = \frac{1+e}{1+e_0}$.

Using material coordinates, the mass balances can be written as follows (Peters and Smith, 2002):

water: $$\frac{\partial}{\partial \tau}\left(\frac{e}{1+e_0}\right) = -\frac{\partial q}{\partial a} \tag{A7a}$$

ions: $$\frac{\partial}{\partial \tau}\left(\frac{e}{1+e_0}\bar{c}_i\right) = -\frac{\partial J_i}{\partial a} \tag{A7b}$$

solid skeleton $$\frac{\partial}{\partial \tau}\left[(1-n)\cdot\frac{1+e}{1+e_0}\right] = 0 \tag{A7c}$$

where $q = n \cdot (v_w - v_{sk})$ and $J_i = n \cdot \bar{c}_i \cdot (v_i - v_{sk})$.

DRAFT

If the hypothesis of infinitesimal strains is assumed, the following approximations can be adopted (Peters and Smith, 2002):

$$\frac{\partial}{\partial \tau} \cong \frac{\partial}{\partial t} \tag{A8a}$$

$$\frac{\partial}{\partial a} \cong \frac{\partial}{\partial x} \tag{A8b}$$

Using approximate relationships A8, mass balances A7a and A7b give mass balances Eqs. 1 of the main text, taking into account that Biot's increment of fluid content ζ is related to the void index e by the following identity: $d\zeta = \frac{de}{1+e_0}$.

Momentum balance equations of the mixture

Neglecting the inertial effects, the momentum balance of the whole mixture, including the solid skeleton (index sk), water (index w) and ion species (index i = 1, 2, … , N), is given by:

$$-\frac{\partial \sigma}{\partial x} + \sum_{r=sk,w,1,2,\ldots}^{N+2} F_r = 0 \tag{A9}$$

where:

F_r = external force per unit volume acting on the components of the system ($N \cdot m^{-3}$).

Taking into account the gravitational and electric fields, the following identification of the external forces is obtained:

$$F_w = n \cdot \rho_w \cdot g \tag{A10a}$$

DRAFT

$$F_i = -n \cdot \bar{c}_i \cdot z_i \cdot F \cdot \frac{\partial \varphi}{\partial x} \qquad \text{for } i = 1, 2, \ldots, N \tag{A10b}$$

$$F_{sk} = (1-n) \cdot \rho_{sk} \cdot g - n \cdot \bar{c}_{sk} \cdot z_{sk} \cdot F \cdot \frac{\partial \varphi}{\partial x} \tag{A10c}$$

where:

ρ_{sk} is the solid skeleton density (kg·m^{-3}) and z_{sk} is the electro-chemical valence of the solid skeleton (which, for bentonite, is expected to be $z_{sk} = -1$).

Considering the electroneutrality condition in the porous medium, and assuming a negative charge for the solid skeleton:

$$\sum_{i=1}^{N} z_i \cdot \bar{c}_i + z_{sk} \bar{c}_{sk} = 0, \tag{A11}$$

Eq. A9 can be expressed as follows:

$$-\frac{\partial \sigma}{\partial x} + \rho \cdot g = 0 \tag{A12}$$

where:

$\rho = (1-n) \cdot \rho_{sk} + n \cdot \rho_w$ = total density of the porous medium (kg·m^{-3}).

Thermodynamic potentials

In order to derive the energy conservation and entropy balance equations for a porous medium whose voids are filled by an electrolyte solution, some fundamental thermodynamics relations, relative to liquid mixtures, need to be taken into account.

DRAFT

The specific internal energy, U_V^f, of the pore solution can be expressed as the sum of the products of the partial molar internal energy times the molar concentration of the solution components:

$$U_V^f = \sum_{k=w,1,2,...}^{N+1} U_k \cdot (n \cdot c_k) \tag{A13}$$

where:

U_V^f = specific internal energy of the pore solution (internal energy per unit volume);

U_k = partial molar internal energy of the k-th pore solution component;

n = porosity;

c_k = molar concentration of the k-th pore solution component.

The first law of thermodynamics states that the variation in the internal energy of a material system is the sum of the mechanical work performed by the external forces on the system and the external heat supply (Coussy, 2004). The first law applied to the components of a liquid mixture that fills the voids of a porous medium can be expressed as follows:

$$dU_k = -u_k \cdot d\left(\frac{1}{c_k}\right) + dQ_k \tag{A14}$$

where $-u_k \cdot d(1/c_k)$ represents the infinitesimal mechanical work supplied to the liquid component by the partial pressure u_k in the infinitesimal volume change $d(1/c_k)$ of its specific material volume $1/c_k$, while dQ_k is the infinitesimal heat supply.

Similarly to what was done for the internal energy, we can introduce the partial molar entropy, S_k, defined as follows:

DRAFT

$$S_V^f = \sum_{k=w,1,2,\ldots}^{N+1} S_k \cdot (n \cdot c_k) \tag{A15}$$

where:

S_V^f = specific entropy of the pore solution (entropy per unit volume);

S_k = partial molar entropy of the k-th pore solution component.

The second law of thermostatics applied to the fluid-specific material volume $1/c_k$ can be expressed in the form:

$$dS_k = \frac{dQ_k}{T} \tag{A16}$$

where T is the absolute temperature.

Eliminating the infinitesimal heat supply, (A14) and (A16) combine to give the following energy balance (Coussy, 2004):

$$dU_k = -u_k \cdot d\left(\frac{1}{c_k}\right) + T \cdot dS_k \tag{A17}$$

Equation A17 holds for any infinitely slow evolution of the liquid from one of its homogeneous equilibrium states to another: as a consequence, $1/c_k$ and S_k constitute a complete set of independent thermodynamic state variables, so that:

$$U_k = U_k\left(\frac{1}{c_k}, S_k\right) \tag{A18}$$

DRAFT

The partial pressure u_k and the absolute temperature can therefore be expressed as derivatives of the partial internal energy with respect to $1/c_k$ and S_k, respectively:

$$u_k = -\frac{\partial U_k}{\partial(1/c_k)} \tag{A19a}$$

$$T = \frac{\partial U_k}{\partial S_k} \tag{A19b}$$

Equations A19a,b are the liquid state equations where the internal energy U_k acts as a potential which links the set of thermodynamic state variables ($1/c_k$, S_k) to the conjugate set ($-u_k$, T) (Coussy, 2004).

Another thermodynamic potential of interest for the next theoretical derivations is the partial molar specific enthalpy, which is defined as follows:

$$H_k = U_k + \frac{u_k}{c_k} \tag{A20}$$

The specific Helmholtz free energy, F_k, of the k-th liquid component can be defined as follows:

$$F_k = U_k - T \cdot S_k \tag{A21}$$

The last thermodynamic potential of interest is the chemical potential, μ_k, which is defined as follows:

DRAFT

$$\mu_k = H_k - T \cdot S_k = U_k + \frac{u_k}{c_k} - T \cdot S_k = F_k + \frac{u_k}{c_k} \tag{A22}$$

The following expression can be derived from Eq. A22 for the infinitesimal increment in chemical potential $d\mu_k$ (Truesdell, 1962):

$$d\mu_k = dU_k + u_k \cdot d\left(\frac{1}{c_k}\right) + \frac{1}{c_k} \cdot du_k - T \cdot dS_k - S_k \cdot dT \tag{A23}$$

Using Eq. A17, Eq. A23 reduces to:

$$d\mu_k = \frac{1}{c_k} \cdot du_k - S_k \cdot dT \tag{A24}$$

where

$du_k / c_k = (d\mu_k)_T$ = chemical potential increment at constant temperature.

The following expression for the increment in the Helmholtz specific free energy can be found from Eqs. A22 and A24:

$$dF_k = -u_k d\left(\frac{1}{c_k}\right) - S_k \cdot dT\,. \tag{A25}$$

At this point, we need to find a suitable state equation for partial pressure u_k, i.e. a relationship with the pore solution component concentrations and the absolute temperature. In order to reach this goal, we can point out that the solute molecules can be assimilated to the particles of an ideal gas under thermal motion (Einstein, 1956; Fermi, 1937). van't Hoff

DRAFT

(1887) first recognized that whenever a solute movement is blocked by a wall, the solute transfers momentum to the wall and therefore generates pressure on it, in analogy with the particles of an ideal gas. The van't Hoff equation is nothing more than the law of perfect gas applied to solute molecules:

$$u_i = R \cdot T \cdot c_i \quad \text{for } i = 1, 2, \ldots, N \tag{A26}$$

where R is the universal gas constant (8.314 $J \cdot mol^{-1} \cdot K^{-1}$).

Considering the additive property of partial pressure, i.e.

$$u = \sum_{k=w,1,2,\ldots}^{N+1} u_k = u_w + \sum_{i=1}^{N} u_i \tag{A27}$$

where u is the liquid pore pressure, the solvent (water) partial pressure u_w can be derived as follows:

$$u_w = u - \sum_{i=1}^{N} u_i \tag{A28}$$

The sum of the solute partial pressures is called the osmotic pressure of the solution and is indicated withy the symbol Π:

$$\Pi = \sum_{i=1}^{N} u_i = R \cdot T \cdot \sum_{i=1}^{N} c_i \, . \tag{A29}$$

DRAFT

The chemical potential increment, at constant temperature, can therefore be expressed, for water and solute (ion) components, respectively, as follows:

$$(d\mu_w)_T = \frac{1}{c_w}(du - d\Pi) \tag{A30a}$$

$$(d\mu_i)_T = \frac{RT}{c_i} dc_i \tag{A30b}$$

Energy balance equation of the mixture

If the kinetic effects are neglected, the energy balance equation of the whole system is given by (Haase, 1990; Heidug and Wong, 1996; Coussy, 2004):

$$\frac{\partial U_V}{\partial t} + \frac{\partial}{\partial x}(U_V v_{sk}) = -\frac{\partial}{\partial x}\left(J_Q + \sigma \cdot v_{sk} + \sum_{k=w,1,2,\ldots}^{N+1} H_k J_k \right) + \sum_{r=sk,w,1,2,\ldots}^{N+2} F_r \cdot v_r \tag{A31}$$

where

U_V = internal energy per unit volume ($J \cdot m^{-3}$);

v_{sk} = velocity of the solid skeleton ($m \cdot s^{-1}$);

J_Q = heat current density ($J \cdot m^{-2} \cdot s^{-1}$);

$J_k = n\bar{c}_k (v_k - v_{sk})$ = relative molar mass flux of the k-the component of the fluid phase with respect to the solid skeleton ($mol \cdot m^{-2} \cdot s^{-1}$)

H_k = partial molar enthalpy of k-th component of the fluid phase ($J \cdot mol^{-1}$);

v_r = velocity of the r-th component of the system ($m \cdot s^{-1}$).

Using Eq. A9, the energy balance (A31) can be rewritten as follows:

DRAFT

$$\frac{\partial U_V}{\partial t}+\frac{\partial}{\partial x}(U_V v_{sk})=-\frac{\partial}{\partial x}\left(J_Q+\sigma\cdot v_{sk}+\sum_{k=w,1,2,..}^{N+1}H_k J_k\right)+\left(v_{sk}\frac{\partial \sigma}{\partial x}+\sum_{k=w,1,2,...}^{N+1}\frac{F_k}{n\bar{c}_k}J_k\right) \tag{A32}$$

Entropy balance of the whole mixture

The entropy balance can be expressed as follows (Haase, 1990; Heidug and Wong, 1996; Coussy, 2004):

$$\frac{\partial S_V}{\partial x}+\frac{\partial}{\partial x}(S_V\cdot v_{sk})\geq-\frac{\partial}{\partial x}\left(\frac{J_Q}{T}+\sum_{k=w,1,2,...}^{N+1}S_k J_k\right) \tag{A33}$$

Then, introducing the Helmholtz free energy of the whole mixture per unit volume, F_V:

$$F_V=U_V-T\cdot S_V \tag{A34}$$

and using the energy balance, Eq. A32, the following inequality is obtained:

$$\begin{aligned}&-\sigma\frac{\partial v_{sk}}{\partial x}-S_V\left[\frac{\partial T}{\partial t}+v_{sk}\frac{\partial T}{\partial x}\right]-\frac{\partial F_V}{\partial t}-\frac{\partial}{\partial x}(F_V v_{sk})+\\&+\sum_{k=w,1,2,.....}^{N+1}\frac{F_k}{n\bar{c}_k}J_k-\frac{\partial}{\partial x}\left(\sum_{k=w,1,2,...}^{N+1}H_k J_k\right)+T\frac{\partial}{\partial x}\left(\sum_{k=w,1,2,...}^{N+1}S_k J_k\right)-\frac{J_Q}{T}\frac{\partial T}{\partial x}\geq 0\end{aligned} \tag{A35}$$

Considering Eq. A22, inequality Eq. A35 can be expressed as follows:

$$\begin{aligned}&-\sigma\frac{\partial v_{sk}}{\partial x}-S_V\left[\frac{\partial T}{\partial t}+v_{sk}\frac{\partial T}{\partial x}\right]-\frac{\partial F_V}{\partial t}-\frac{\partial}{\partial x}(F_V v_{sk})-\sum_{k=w,1,2,...}^{N+1}\mu_k\frac{\partial J_k}{\partial x}+\\&+\sum_{k=w,1,2,.....}^{N+1}\frac{F_k}{n\bar{c}_k}J_k-\sum_{k=w,1,2,...}^{N+1}\left(\frac{\partial \mu_k}{\partial x}-S_k\frac{\partial T}{\partial x}\right)J_k-\frac{J_Q}{T}\frac{\partial T}{\partial x}\geq 0\end{aligned} \tag{A36}$$

DRAFT

Inequality Eq. A36 is a generalization to a pore solution containing N ion species of the inequality obtained by Coussy (1995) for a porous medium saturated by a mono-component liquid. According to Coussy (1995 and 2004), three distinct sources of dissipation can be identified:

$$\Phi_s = -\sigma\frac{\partial v_{sk}}{\partial x} - S_V\left[\frac{\partial T}{\partial t} + v_{sk}\frac{\partial T}{\partial x}\right] - \frac{\partial F_V}{\partial t} - \frac{\partial}{\partial x}\left(F_V v_{sk}\right) - \sum_{k=w,1,2,\ldots}^{N+1}\mu_k\frac{\partial J_k}{\partial x} \tag{A37a}$$

$$\Phi_f = \sum_{k=w,1,2,\ldots.}^{N+1}\frac{F_k}{n\bar{c}_k}J_k - \sum_{k=w,1,2,\ldots}^{N+1}\left(\frac{\partial \mu_k}{\partial x} - S_k\frac{\partial T}{\partial x}\right)J_k \tag{A37b}$$

$$\Phi_{th} = -\frac{J_Q}{T}\frac{\partial T}{\partial x} \tag{A37c}$$

where

Φ_s represents the solid skeleton dissipation, Φ_f accounts for the fluid dissipation and Φ_{th} is related to the dissipation due to heat conduction.

If the solid skeleton is assumed to behave as an elastic body, $\Phi_s = 0$ and inequality Eq. A36 reduces to:

$$\Phi = \Phi_f + \Phi_{th} = -\frac{J_Q}{T}\frac{\partial T}{\partial x} + \sum_{k=w,1,2,\ldots}^{N+1}J_k\left[\frac{F_k}{n\bar{c}_k} - \left(\frac{\partial \mu_i}{\partial x}\right)_T\right] \geq 0 \tag{A38}$$

where Φ represents the total dissipation. The chemical potential gradient at constant temperature, as defined in Eq. A24, has been introduced into Eq. A38.

For isothermal systems $(dT = 0)$, the dissipation function Φ can be expressed as follows:

DRAFT

$$\Phi = -n\bar{c}_w (v_w - v_{sk}) \left[\left(\frac{\partial \mu_w}{\partial x} \right)_T - \frac{F_w}{n\bar{c}_w} \right] - \sum_{i=1}^{N} n\bar{c}_i (v_i - v_{sk}) \left[\left(\frac{\partial \mu_i}{\partial x} \right)_T - \frac{F_i}{n\bar{c}_w} \right] \tag{A39}$$

Using Eqs. A2, A10 and A30a, the dissipation function Φ can be expressed as in Eq. 6 of the main text:

$$\Phi = -q \cdot \left(\frac{\partial u}{\partial x} - \frac{\partial \Pi}{\partial x} - \rho_w g \right) - \sum_{i=1}^{N} J_i \cdot \left(\frac{\partial \mu_i^{ec}}{\partial x} \right) \tag{A40}$$

where:

$d\mu_i^{ec} = (d\mu_i)_T + z_i F \cdot d\varphi$ = differential of the electro-chemical potential of the i-th ion.

The dissipation term Φ_s is null for an elastic solid skeleton and the following balance of the Helmholtz free energy can be derived from Eq. A37a:

$$\frac{\partial F_V}{\partial t} + \frac{\partial}{\partial x}(F_V v_{sk}) + S_V \cdot \left[\frac{\partial T}{\partial t} + v_{sk} \frac{\partial T}{\partial x} \right] = -\sigma \frac{\partial v_{sk}}{\partial x} - \sum_{k=w,1,2,\ldots}^{N+1} \mu_k \frac{\partial J_k}{\partial x} \tag{A41}$$

Introducing the material derivative:

$$\frac{d}{dt} = \frac{\partial}{\partial \tau} = \frac{\partial}{\partial t} + v_{sk} \frac{\partial}{\partial x} \tag{A42}$$

the Helmholtz free energy balance can be written as follows:

$$\frac{dF_V}{dt} + F_V \frac{\partial v_{sk}}{\partial x} + S_V \frac{dT}{dt} = -\sigma \cdot \frac{\partial v_{sk}}{\partial x} - \sum_{k=w,1,2,\ldots}^{N+1} \mu_k \frac{\partial J_k}{\partial x} \tag{A43}$$

DRAFT

It is convenient to work with the so-called energy function $\Im_V$, which is defined as follows

$$\Im_V = J \cdot F_V \tag{A44}$$

which represents the Helmholtz free energy of the mixture per unit initial volume.

Observing that

$$\frac{dJ}{dt} = J \frac{\partial v_{sk}}{\partial x} \tag{A45}$$

the material derivative of $\Im_V$ results to be given by:

$$\frac{d\Im_V}{dt} = J \cdot \left(\frac{dF_V}{dt} + F_V \frac{\partial v_{sk}}{\partial x} \right) \tag{A46}$$

Introducing the energy function $\Im_V$ into the Helmholtz free energy balance, Eq. A43, it is possible to derive the following equation:

$$\frac{d\Im_V}{dt} + \Sigma_V \cdot \frac{dT}{dt} = -\sigma \cdot \left(J \frac{\partial v_{sk}}{\partial x} \right) - \sum_{k=w,1,2,\ldots}^{N+1} \mu_k \cdot \left(J \frac{\partial J_k}{\partial x} \right) \tag{A47}$$

or, using Eq. A6

$$\frac{d\Im_V}{dt} + \Sigma_V \cdot \frac{dT}{dt} = -\sigma \cdot \left(\frac{\partial v_{sk}}{\partial a} \right) - \sum_{k=w,1,2,\ldots}^{N+1} \mu_k \cdot \left(\frac{\partial J_k}{\partial a} \right) \tag{A48}$$

DRAFT

where Σ represents the entropy of the mixture per unit initial volume.

If, at this point, the assumption of small strains is introduced, the following approximations hold:

$$\frac{d\Im_V}{dt} \cong \frac{\partial \Im_V}{\partial t} \tag{A49a}$$

$$\frac{dT}{dt} \cong \frac{\partial T}{\partial t} \tag{A49b}$$

$$\frac{\partial v_{sk}}{\partial a} \cong \frac{\partial v_{sk}}{\partial x} = -\frac{\partial \varepsilon}{\partial t} \tag{A49c}$$

$$\frac{\partial J_k}{\partial a} \cong \frac{\partial J_k}{\partial x} = -\frac{1}{1+e_0}\frac{\partial (e \cdot \bar{c}_k)}{\partial t} \tag{A49d}$$

For infinitesimal strains, we can write the following expression for the energy function increment $d\Im_V$:

$$d\Im_V = -\Sigma \cdot dT + \sigma \cdot d\varepsilon + \sum_{k=w,1,2,\ldots}^{N+1} \mu_k \frac{d(e \cdot \bar{c}_k)}{1+e_0} \tag{A50}$$

According to Coussy (1995 and 2004) and Dormieux et al. (2003), the Helmholtz free energy of the solid skeleton relative to the initial or undeformed volume, $\Im_V^{sk}$, can be derived by subtracting, from the free energy of mixture $\Im_V$, the free energy of the real fluid phase $\Im_V^f$, which is defined as follow:

$$\Im_V^f = \frac{e}{1+e_0} \sum_{k=w,1,2,\ldots}^{N+1} (\bar{c}_k \cdot F_k) \tag{A51}$$

DRAFT

Therefore, $\mathfrak{I}_V^{sk}$ results given by:

$$\mathfrak{I}_V^{sk} = \mathfrak{I}_V - \mathfrak{I}_V^{f} \tag{A52}$$

Using Eqs. A22, A24, A25 and A50, the infinitesimal increment $d\mathfrak{I}_V^{sk}$ is given by:

$$d\mathfrak{I}_V^{sk} = -\Sigma^{sk} \cdot dT + \sigma \cdot d\varepsilon + \sum_{k=w,1,2,\ldots}^{N+1} u_k \frac{1}{1+e_0} d\left(\frac{e \cdot \bar{c}_k}{c_k}\right) \tag{A53}$$

where $\Sigma^{sk} = \Sigma - \Sigma^{f}$ is the entropy per unit initial volume of the solid skeleton, which is obtained as the difference between the entropy of the mixture, Σ, and the entropy of the fluid phase $\Sigma^{f} = \frac{e}{1+e_0} \sum_{k=w,1,2,\ldots}^{N+1} (\bar{c}_k \cdot S_k)$.

Eq. A53 can be re-written by separating the water and ion contributions and observing that $\bar{c}_w = c_w$, due to the fact that water is constituted by uncharged molecules and, for this reason, does not undergo a partition effect, therefore

$$d\mathfrak{I}_V^{sk} = -\Sigma^{sk} \cdot dT + \sigma \cdot d\varepsilon + u_w \frac{de}{1+e_0} + \sum_{i=1}^{N} \frac{u_i}{1+e_0} d\left(\frac{e \cdot \bar{c}_i}{c_i}\right) \tag{A54}$$

Using Eq. 2, 3 and A28, $d\mathfrak{I}_V^{sk}$ can be expressed as follows:

$$d\mathfrak{I}_V^{sk} = -\Sigma^{sk} \cdot dT + \left[\sigma - (u - \Pi)\right] \cdot d\varepsilon + \sum_{i=1}^{N} \frac{u_i}{1+e_0} d\left(\frac{e \cdot \bar{c}_i}{c_i}\right) \tag{A55}$$

DRAFT

where u is the hydraulic pressure of the fluid phase and $\Pi = \sum_{i=1}^{N} u_i = RT \cdot \sum_{i=1}^{N} c_i$ is the osmotic pressure of the virtual solution.

In the absence of a partition effect, also for the ions, i.e. $\bar{c}_i = c_i$, Eq. A55 reduces to the classical form obtained by Coussy (1995):

$$d\Im_V^{sk} = -\Sigma^{sk} \cdot dT + (\sigma - u) \cdot d\varepsilon \tag{A56}$$

where $\sigma' = (\sigma - u)$ represents the effective stress.

Poro-elastic constitutive equations, can be derived, under isothermal conditions (i.e. dT = 0), from Eq. A55, considering $\Im_V^{sk}$ as a function of ε and $(e \cdot \bar{c}_i / c_i)$. As an alternative, it can be convenient to work with the Legendre transform of $\Im_V^{sk}$, which is defined as follows:

$$\Im_V^{sk\prime} = \left[\sigma - (u - \Pi)\right] \cdot \varepsilon + \sum_{i=1}^{N} \frac{e}{1+e_0} u_i \frac{\bar{c}_i}{c_i} - \Im_V^{sk}. \tag{A57}$$

Using Eq. A55, the differential of $\Im_V^{sk\prime}$, for isothermal systems, is given by:

$$d\Im_V^{sk\prime} = \varepsilon \cdot \left[d\sigma - (du - d\Pi)\right] + \sum_{i=1}^{N} \frac{e \cdot \bar{c}_i}{1+e_0} \frac{du_i}{c_i}. \tag{A58}$$

Using Eq. A24 with dT = 0, the expression of $d\Im_V^{sk\prime}$ can be formulated as follows:

DRAFT

$$d\Im_V^{sk\,\prime} = \varepsilon \cdot \left[d\sigma - (du - d\Pi) \right] + \sum_{i=1}^{N} \frac{e \cdot \bar{c}_i}{1 + e_0} (d\mu_i)_T \tag{A59}$$

and the equation that has been introduced into the main text as Eq. 28 for the derivation of the poro-elastic constitutive equations is obtained.

DRAFT

APPENDIX B

The assumption of ideal, i.e. infinitely diluted, solution is generally acceptable when dealing with natural soil water or landfill leachate. However, in some cases, relatively high ion concentrations can be encountered, as in the case of the proximity of sea water, therefore such an assumption cannot be adopted and corrective terms need to be introduced into the theoretical approach described in the paper.

In the case of high ion concentrations, the ion chemical potential increment at constant temperature can be expressed as follows (Helfferich, 1962; Katchalsky and Curran, 1965; Samson et al., 1999):

$$(d\mu_i)_T = \frac{RT}{\gamma_i c_i} d(\gamma_i c_i) \tag{B1}$$

where:

γ_i = activity coefficient (-), by which c_i is multiplied to give the "active concentration" or activity, a_i:

$$a_i = \gamma_i \cdot c_i \tag{B2}$$

The osmotic pressure increment, $d\Pi$, results to be related to the ion concentration increments as follows:

$$d\Pi = \sum_{i=1}^{N} c_i (d\mu_i)_T = RT \sum_{i=1}^{N} \frac{1}{\gamma_i} d(\gamma_i c_i). \tag{B3}$$

DRAFT

The activity coefficient, γ_i, is an experimentally determinable function of the concentration of all the ions contained in the aqueous solution.

In the case of only one salt being present in the aqueous solution, the ion activity coefficients can be related to only the salt concentration c_s, since the ion concentrations are linked to each other through the electroneutrality condition, $\sum_{i=1}^{2} z_i c_i = 0$. The salt chemical potential increment at constant temperature, given by Eq. 17, can therefore be related to the salt concentration as follows:

$$(d\mu_s)_T = \frac{1}{c_s} d\Pi = \nu_1 \cdot (d\mu_1)_T + \nu_2 \cdot (d\mu_2)_T = RT \left[\frac{(\nu_1 + \nu_2)}{c_s} + \nu_1 \frac{d \ln \gamma_1}{dc_s} + \nu_2 \frac{d \ln \gamma_2}{dc_s} \right] dc_s . \qquad \text{(B3)}$$

Eq. B1 can be used to relate the chemical potential at constant temperature to the ion concentration in substitution of Eq. A30b, when the concentration is too high to make the assumption of ideal solution acceptable. Similarly, taking into account Eq. B3, the solute permeability, P_s, results to be related to the phenomenological coefficients α_{ss}, α_{sw}, α_{ww} through the following expression:

$$P_s = \left(\alpha_{ss} - \frac{\alpha_{sw}^2}{\alpha_{ww}} \right) \left[\frac{(\nu_1 + \nu_2)}{c_s} + \nu_1 \frac{d \ln \gamma_1}{dc_s} + \nu_2 \frac{d \ln \gamma_2}{dc_s} \right] . \qquad \text{(B4)}$$

DRAFT

REFERENCES

Auclair, B., Nikonenko, V., Larchet, C., Métayer, M., and Dammak, L., 2002. Correlation between transport parameters of ion-exchange membranes. Journal of Membrane Science, 195, 89-102.

Barbour, S., and Fredlund, D., 1989. Mechanisms of osmotic flow and volume change in clay soils. Canadian Geotechnical Journal, 26, 551–562.

Bear, J., 1972. Dynamics of fluids in porous media. American Elsevier, New York, N.Y.

Biot M.A., 1941. General theory of three-dimensional consolidation. Journal of Applied Physics, 12 (2), 155-164.

Biot, M.A., 1972. Theory of finite deformation of porous solids, Indiana University Mathematical Journal, 24, 579-620.

Biot, M.A., 1977. Variational Lagrangian-thermodynamics of non isothermal finite strain. Mechanics of porous solid and thermomolecular diffusion. International Journal of Solids and Structures, 13 (6), 579-597.

Bouazza, A., 2002. Geosynthetic clay liners. Geotextiles and Geomembranes, 20, 3-17.

Coleman, B.D., and Noll, W., 1963. The thermodynamics of elastic materials with heat conduction and viscosity. Archive for Rational Mechanics and Analysis, 13, 167–178.

Coussy, O., 1995. Mechanics of porous continua. John Wiley & Sons, Chichester, England.

Coussy, O., 2004. Poromechanics. John Wiley & Sons, Chichester, England.

De Boer, R., 2000. Theory of Porous Media: Highlights in the historical development and current state. Springer-Verlag, Berlin – Heidelberg - New York.

De Boer, R., 2005. Trends in continuum mechanics of porous media. Springer, Dordrecht, The Netherlands.

De Groot, S.R., and Mazur, P., 1962. Non-equilibrium Thermodynamics, North-Holland, Amsterdam.

DRAFT

Dominijanni, A., and Manassero, M., 2010. Chemico-osmosis and solute transport through geosynthetic clay liners. In: Geosynthetic clay liners for waste containment, Bouazza A., Bowders J.J. (Eds.), CRC Press, 105-125.

Dominijanni, A., and Manassero, M., 2011. Modelling the swelling and osmotic properties of caly soils: Part II. The physical approach, *submitted for publication*.

Donnan, F.G., 1911. Theorie der Membrangleichgewichte und Membranpotentiale bei Vorhandensein von nicht dialysierenden Elektrolyten. Ein Beitrag zur physikalisch-chemischen Physiologie [Theory of membrane equilibria and membrane potentials in the presence of non-dialysing electrolytes. A contribution to physical-chemical physiology], Zeitschrift für Elektrochemie und angewandte physikalische Chemie, 17, 572-581. English translation republished in Journal of Membrane Science, 100 (1995), 45-55.

Dormieux, L., Barboux, P., Coussy, O., and Dangla, P., 1995. A macroscopic model of the swelling phenomenon of a saturated clay. European Journal of Mechanics A/Solids, 14 (6), 981-1004.

Dormieux, L., Lemarchand, E., and Coussy, O., 2003. Macroscopic and micromechanical approaches to the modelling of the osmotic swelling in clays. Transport in Porous Media, 50, 75-91.

Eckart, C., 1940a. The thermodynamics of irreversible processes. I. The simple fluid. Physical Review, 58, 267-269.

Eckart, C., 1940b. The thermodynamics of irreversible processes. II. Fluid mixtures. Physical Review, 58, 269-275.

Ehlers, W., 2002. Foundations of multiphasic and porous materials, in: Ehlers, W., and Bluhm, J., (Eds.), Porous Media: Theory, Experiments and Numerical Applications. Springer-Verlag, Berlin, 3–86.

DRAFT

Einstein, A., 1956. Investigations on the theory of the Brownian movement. Dover Publications., New York.

Fermi, E., 1937. Thermodynamics. Prentice-Hall, republished by Dover Publications in 1956.

Freeze, R.A., and Cherry, J.A., 1979. Groundwater, Prentice-Hall, Englewood Cliffs, N.J.

Gibson, R.E., England, G.L., and Hussey, M.J.L., 1967. The theory of one-dimensional consolidation of saturated clays. Géotechnique, 17 (3), 261-273.

Haase, R., 1990. Thermodynamics of Irreversible Processes, Dover, New York.

Heidug, W.K., and Wong S.-W., 1996. Hydration swelling of water-absorbing rocks: a constitutive model. Journal for Numerical and Analytical Methods in Geomechanics, 20 (6), 403-430.

Helfferich, F., 1962. Ion exchange, McGraw-Hill, New York.

Kaczmarek, M., and Hueckel, T., 1998. Chemo-mechanical consolidation of clays: analytical solutions for a linearized onedimensional problem. Transport in Porous Media, 32, 49-74.

Katchalsky, A., and Curran, P.F., 1965. Nonequilibrium thermodynamics in biophysics. Harvard University Press, Cambridge, MA.

Kemper, W.D., and Quirk, J.P., 1972. Ion mobilities and electric charge of external clay surfaces inferred from potential differences and osmotic flow. Soil Science Society of America Proceedings, 36, 426-433.

Letey, J., and Kemper, 1969. Movement of salt and water through a clay-water system: experimental verification of Onsager reciprocal relation. Soil Science Society of America Proceedings, 33, 25-29.

Malusis, M.A., and Shackelford C.D., 2002. Theory for reactive solute transport through clay membrane barriers. Journal of Contaminant Hydrology, 59 (4-4), 291-316.

DRAFT

Malusis, M.A., Shackelford, C.D., and Olsen, H.W., 2001. A laboratory apparatus to measure chemico-osmotic efficiency coefficients for clay soils. Geotechnical Testing Journal, 24 (3), 229-242.

Meixner, J., and Reik, H.G., 1959. Die Thermodynamik der irreversiblen Prozesse in kontinuierlichen Medien mit inneren Umwandlungen [Thermodynamics of irreversible processes in continuous media with internal transformations], In, Flügge, S., Handbuch der Physik, Bd. III/2, Springer Heidelberg.

Mitchell, J. K., 1993. Fundamentals of Soil Behavior, 2nd ed., Wiley, New York.

Neuzil, C.E., 1986. Groundwater flow in low-permeability environments. Water Resources Research, 22 (8), 1163-1195.

Onsager, L., 1931a, Reciprocal relations in irreversible processes I. Physical Review, 37 (4), 405-426.

Onsager, L., 1931b, Reciprocal relations in irreversible processes II. Physical Review, 38 (12), 2265-2279.

Peters, G.P., and Smith, D.W., 2002. Solute transport through a deforming porous medium. International Journal for Numerical and Analytical Methods in Geomechanics, 26, 683-717.

Peters, G.P., and Smith, D.W., 2004. The influence of advective transport on coupled chemical and mechanical consolidation of clays. Mechanics of Materials, 36, 467-486.

Philip, J.R., and Smiles, D.E., 1982. Macroscopic analysis of the behaviour of colloidal suspensions. Advances in Colloid and Interface Science, 17, 83-103.

Prigogine, I., 1947. Etude thermodynamique des Phenomenes Irreversibles. Desoer, Liege.

Raats, P.A.C., and Klute, A., 1968a. Transport in soils: The balance of mass. Soil Science Society of America Proceedings, 32 (2), 161-166.

DRAFT

Raats, P.A.C., and Klute, A., 1968b. Transport in soils: The balance of momentum. Soil Science Society of America Proceedings, 32 (4), 452-456.

Rajagopal, K.R., and Tao, L., 1995. Mechanics of mixtures. World Scientific, Singapore.

Revil, A., 2007. Thermodynamics of ions and water transport in porous media. Journal of Colloid and Interface Science, 307, 254-264.

Robinson, R.A., and Stokes, R.H., 1959. Electrolyte solutions, 2nd Ed., Butterworths Scientific Publications, London, England.

Samson, E., Lemaire, G., Marchand, J., and Beaudoin, J.J., 1999. Modeling chemical activity effects in strong ionic solutions. Computetional M;aterials Science, 15, 285-294.

Shackelford, C.D., 1989. Diffusion of contaminants through waste containment barriers. Transportation Research Record, 1219, 169-182.

Shackelford, C.D., 1993. Contaminant Transport. In Geotechnical Practice for Waste Disposal, D.E. Daniel, ed., Chapman and Hall, London.

Sherwood, J.D., 1993. Biot poroelasticity of a chemically active shale. Proceedings of the Royal Society of London A, 440 (1909), 365-377.

Smiles, D.E., 2008. Effects of solutes on clay-water interactions: Some comments. Applied Clay Science, 42 (1-2), 158-162.

Smiles, D.E., and Rosenthal, M.J., 1968. The movement of water in swelling materials, Australian Journal of Soil Research, 6 (2), 237-248.

Spiegler, K.S., and Kedem, O., 1966. Thermodynamics of hyperfiltration (reverse osmosis): criteria for efficient membranes. Desalination, 1, 311-326.

Staverman, A.J., 1952. Non-equilibrium thermodynamics of membrane processes. Transactions of the Faraday Society, 48 (2), 176-185.

Truesdell, C., 1962. Mechanical basis of diffusion. The Journal of Chemical Physics, 37, 2336-2344.

DRAFT

Truesdell, C., 1984a. Thermodynamics of diffusion. In: "Rational thermodynamics", Truesdell C. (Ed.), Springer-Verlag, 219-236.

Truesdell, C., 1984b. The Onsager relations. In: "Rational thermodynamics", Truesdell C. (Ed.), Springer-Verlag, 365-395.

Truesdell, C., and Toupin, R.A., 1960. The classical field theories, in: Flügge, S., (Ed.), Handbuch der Physik, vol. III/1, Springer-Verlag, Berlin, 226–902.

van't Hoff, J. H., 1887. The role of osmotic pressure in the analogy between solutions and gases. Zeitschrift fur physikalische Chemie, Vol. 1, 481-508.

Yaroshchuk, A.E., 1995. Osmosis and reverse osmosis in fine-charged diaphragms and membranes. Advances in Colloid and Interface Science, 60, 1-93.

Yeung, A.T-C., and Mitchell, J.K., 1993. Coupled fluid, chemical, and electrical flows in soil, Geotechnique, 43 (1), 121-134.

DRAFT

LIST OF FIGURES

DRAFT

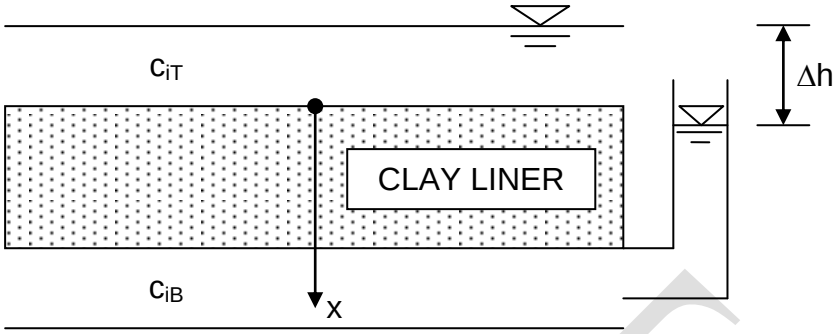

Figure 1. Reference problem representing a horizontal clay barrier separating two electrolyte solutions containing different ion concentrations. Symbols: c_{iT} = concentration of the i-th ion in the solution at the top of the liner; c_{iB} = concentration of the i-th ion in the solution at the bottom of the liner; Δh = difference in the hydraulic head between the top and bottom electrolyte solutions; x = spatial coordinate.

DRAFT

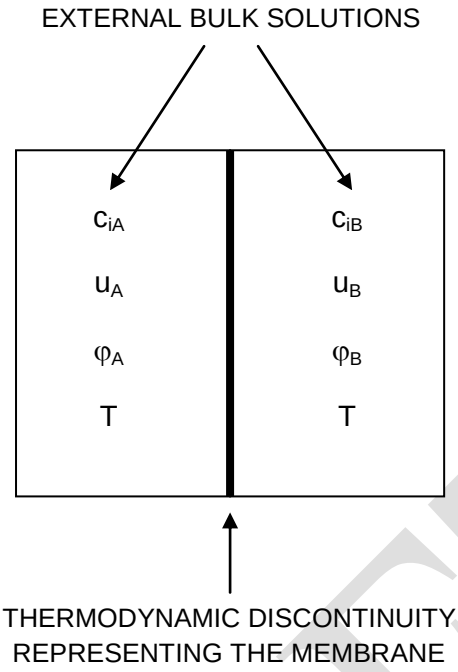

Figure 2. Conceptual scheme of the Staverman (1952) model. Subscript A and B refer to the electrolyte solution reservoirs on the left and on the right of the thermodynamic discontinuity, that represents the membrane. Symbols: c_i = ion concentration of the i-th ion; u = hydraulic pressure; φ = electric potential; T = absolute temperature.

DRAFT

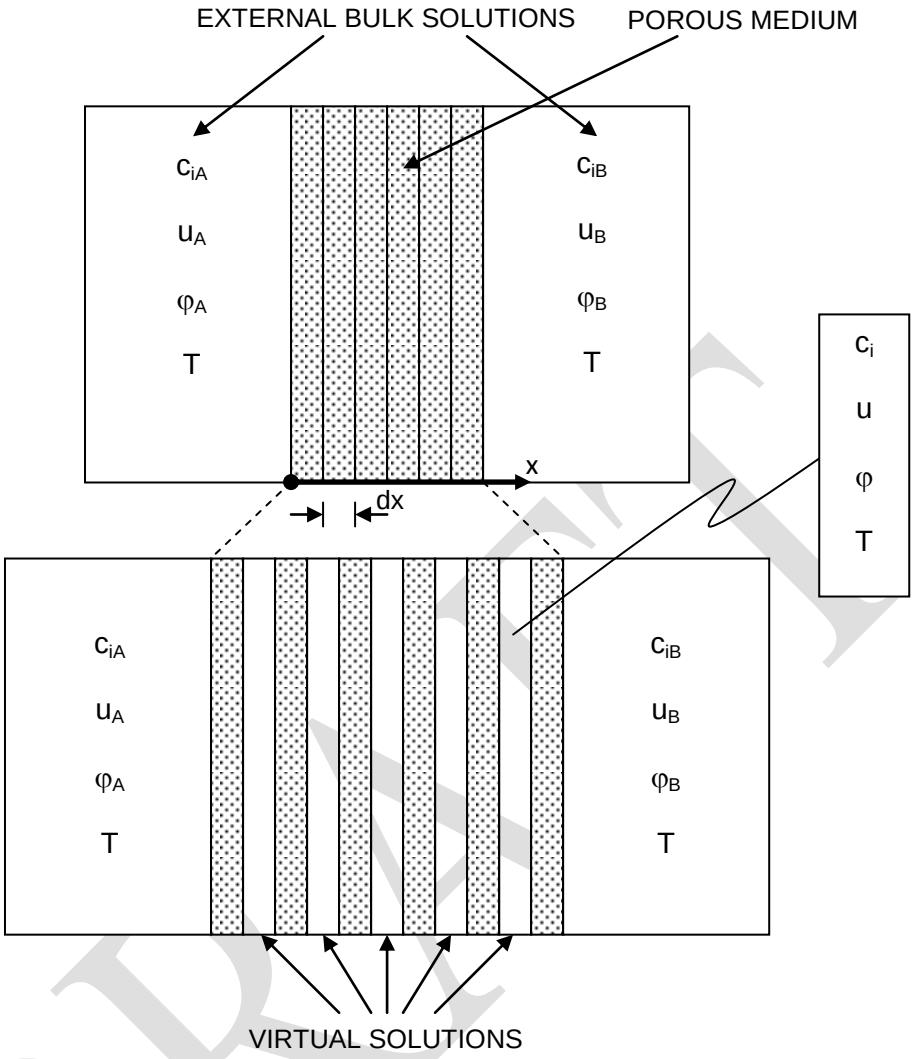

Figure 3. Conceptual scheme of the Spiegler and Kedem (1966) model. Subscript A and B refer to the electrolyte solution reservoirs on the left and on the right of the thermodynamic discontinuity, that represents the membrane. Symbols: c_i = ion concentration of the i-th ion; u = hydraulic pressure; φ = electric potential; T = absolute temperature.

DRAFT